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# CO<sub>2</sub>-Triggered Switchable Hydrophilicity of Heterogeneous Conjugated Polymer Photocatalyst for Enhanced Catalytic Activity in Water

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Abstract: Water-compatibility of heterogeneous photocatalysts has been pursued for energy and environmental applications. However, there exists a trade-off between hydrophilicity and recyclability of the photocatalyst. Herein, we report a conjugated polymer photocatalyst with tertiary amine terminals that reversibly binds CO<sub>2</sub> in water, generating a switchable hydrophilicity. The CO2-assisted hydrophilicity boosted up the photocatalytic efficiency in aqueous medium with minimum dosage. When CO2 was desorbed, the photocatalyst could be simply regenerated from reaction media, of photocatalyst. facilitating the repeated use The hydrophilicity/hydrophobicity control of the polymer photocatalyst has successfully showcased through a variety of organic photo-redox reactions under visible light irradiation in water.

Conjugated polymers have emerged as a new generation of heterogeneous photocatalysts for utilizing visible light as a cheap and environmentally-friendly energy source<sup>[1]</sup>. By virtue of structural robustness, non-toxicity, and high photocatalytic efficiency, the conjugated polymer photocatalysts have been suggested as a sustainable alternative to resolve a chronic drawback of small molecular photocatalysts, i.e., transition-metal complexes<sup>[2]</sup> and organic dyes<sup>[3]</sup>. Due to the fact of being a polymer, the conjugated polymer photocatalysts can be designed for target application, in which their electronic, optical, and chemical properties can be tuned by doping method<sup>[4]</sup>, molecular engineering<sup>[5]</sup>, surface functionalization<sup>[6]</sup> etc. In this regard, there has been an enormous effort to construct efficient polymer photocatalysts, to name a few, carbon nitride<sup>[7]</sup>, conjugated microporous polymer<sup>[8]</sup>, covalent triazine framework<sup>[9]</sup>, and polymer<sup>[10]</sup>, planarized conjugated conducting polymer nanostructure<sup>[11]</sup>.

Besides the material design viewpoint, a more facile approach to environmentally-friendly reaction would be a utilization of green solvents. Water, in particular, is considered as a cheap, safe, and eco-friendly green solvent for chemical reactions<sup>[12]</sup>. Furthermore, the employment of water opens up a potential for energy, environmental, and biological applications such as water splitting<sup>[7b, 13]</sup>, anti-bacterial treatment<sup>[4b]</sup>, photodynamic therapy<sup>[14]</sup>, and water treatment<sup>[6, 11a]</sup>. Accordingly, water-compatible heterogeneous polymer photocatalysts have been recently achieved through transformation<sup>[4b, 13b]</sup>, surface functionalization<sup>[6, 15]</sup>, and protonation via acid treatment<sup>[16]</sup>. However, such synthetic protocols accompanied a permanent wettability change of

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photocatalysts, which may cause difficulty in recovering and regenerating the photocatalyst after reaction. Indeed, there has been a trade-off between water-compatibility and efficient recovery of photocatalyst.

One strategy for making water-compatible photocatalyst without compromising its recyclability is to apply 'switchable' hydrophilicity to polymer photocatalyst. In other words, the wettability of polymer photocatalyst is reversibly switched from hydrophilic to hydrophobic depending on reaction sequence. Lately, CO2 gas, as an abundant and cheap reagent, has been realized as an external stimulus for controlling wettability of materials such as membrane<sup>[17]</sup>, colloid dispersion<sup>[18]</sup>, solvent<sup>[19]</sup>, surfactant<sup>[20]</sup>, polymer nanoparticle<sup>[21]</sup>, block copolymer<sup>[22]</sup>, and small molecular homogenous catalyst<sup>[23]</sup>. The CO<sub>2</sub>-responsive functional groups, i.e. amidine, guanidine and amine, can reversibly form a charged cation by binding CO2 in a presence of water, resulting in better wettability of the materials. Notwithstanding the effectiveness, CO<sub>2</sub>-assisted hydrophilicity control of heterogeneous photocatalytic system has yet been unveiled.

Herein, we aim to control the hydrophilicity of heterogeneous conjugated polymer photocatalysts in water by a simple  $CO_2/N_2$  switch. A tertiary amine-tethered conjugated polymer was designed to exhibit a reversible hydrophilicity change triggered by  $CO_2$ , which enhances its photocatalytic efficiency and recyclability in water. The polymer photocatalysts having switchable hydrophilic nature were demonstrated for photocatalytic reactions in aqueous medium under visible light illumination, i.e. photodegradation of organic dyes and organic transformations of water-soluble molecules.



Scheme 1. Schematic illustration of the switchable hydrophilicity and the photocatalytic applications of the conjugated polymer photocatalyst in water by  $CO_2/N_2$  swing.

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The reversible hydrophilicity/hydrophobicity of the conjugated polymer photocatalyst is illustrated in Scheme 1. The conjugated polymer P-BT-DEA bearing tertiary amine was simply generated through post-modification of hydrophobic P-BT-Br with diethylamine (DEA) (Figure S1). Elemental analysis indicated a 91.3 % conversion of bromine on P-BT-Br to amine on P-BT-DEA (Table S1). As revealed in Figure 1a, the P-BT-DEA stays hydrophobic in water, however once being treated with CO<sub>2</sub> gas for 1 h, DEA at the terminal of the polymer bound CO<sub>2</sub>, producing bicarbonate salt in a presence of water. The formation of bicarbonate salt boosts up water compatibility of the polymeric chain, leading to good polymer dispersion in water (the solution was named as P-BT-DEA-CO<sub>2</sub> hereafter). The absorbed CO<sub>2</sub> can be removed by N<sub>2</sub> treatment under mild condition, and the elimination of bicarbonate salt causes precipitation of hydrophobic P-BT-DEA which can be filtered through normal paper filter (Figure S2). Such a switchable hydrophilicity could be also observed in two-dimensional system, in which P-BT-DEA film on glass substrate exhibited smaller contact angle after the treatment with CO<sub>2</sub> in water (Figure 1b).



**Figure 1.** (a) Photographs of P-BT-DEA in water showing switchable hydrophilicity/hydrophobicity. (b) Contact angle of P-BT-DEA film before and after CO<sub>2</sub> treatment for 1 h in H<sub>2</sub>O. (c) Reversible zeta potential of P-BT-DEA dispersion in water by CO<sub>2</sub>/N<sub>2</sub> treatment and concurrent pH change. FT-IR spectra of (d) P-BT-Br, (e) P-BT-DEA, (f) P-BT-DEA-CO<sub>2</sub>, and (g) regenerated P-BT-DEA after N<sub>2</sub> treatment.

The CO<sub>2</sub>-assisted wettability change could be monitored by zeta potential change of polymer dispersion in water. As shown in Figure 1c, the original P-BT-DEA exhibited ca. 3 mV of zeta potential in water, indicating unstable colloid with a rapid flocculation behavior<sup>[24]</sup>. On the other hand, the P-BT-DEA-CO<sub>2</sub> showed c.a. 20 mV of zeta potential, demonstrating the increase of dispersion stability due to the CO<sub>2</sub>-triggered hydrophilicity. The zeta potential displayed a reversible pattern with respect to CO<sub>2</sub> and N<sub>2</sub> swing, implying that the P-BT-DEA-CO<sub>2</sub> can be recycled for repeated use. There existed obvious pH change of P-BT-DEA aqueous solution under the CO<sub>2</sub>/N<sub>2</sub> shift (Figure 1c). The initial pH of P-BT-DEA in water was about 8.4, which further went down to

5.5 during the CO<sub>2</sub> treatment owing to the formation of carbonic acid (H<sub>2</sub>CO<sub>3</sub>). The pH of the aqueous polymer dispersion was recovered to 8.25 under N<sub>2</sub> condition, which indicates all the CO<sub>2</sub> was desorbed from the solution. The pH change was also reversible under the different gas atmosphere. The dynamic light scattering (DLS) of aqueous P-BT-DEA-CO<sub>2</sub> gave an average diameter of 339 ± 96 nm, corresponding to the microscopic observation (Figure S3).

The reversible formation of bicarbonate salt on P-BT-DEA was able to be monitored with FT-IR spectroscopy (Figure 1d-g). A stretching vibration of C-Br at 560 cm<sup>-1</sup> was disappeared on P-BT-DEA, indicating a complete amination (Figure 1d). The P-BT-DEA showed three peaks at 1200, 1365, and 2790 cm<sup>-1</sup>, which are attributed to tertiary aliphatic amine C-N stretching, N-CHdeformation, and N-CH<sub>3</sub> stretching vibration, respectively (Figure 1e). As Figure 1f shows, when treated with CO<sub>2</sub> in water, the P-BT-DEA-CO<sub>2</sub> displayed intense peaks at 1635 and 3350 cm<sup>-1</sup> which correspond to HCO3<sup>-</sup> (aq.)<sup>[25]</sup> and OH stretching vibration, respectively. As the bicarbonate peak was evolved, the peaks from DEA were weakened, which may be originated from a shielding effect of bicarbonate ion at the position of DEA<sup>[26]</sup>. Once the P-BT-DEA-CO<sub>2</sub> was regenerated with N<sub>2</sub>, the FT-IR spectrum became identical to that of pristine P-BT-DEA (Figure 1g). The formation of bicarbonate on P-BT-DEA was also observed by <sup>13</sup>C NMR spectrum (Figure S4).

The UV-vis diffuse reflectance (DR) spectrum of P-BT-DEA showed a broad absorption in the visible region up to 560 nm (Figure S5a), which is a typical behavior of benzothiadiazole (BT)-anchored porous conjugated polymer photocatalysts<sup>[27]</sup>. The optical band gap (E<sub>g</sub>) of 2.19 eV was derived from the Kubelka-Munk-transformed reflectance spectrum of P-BT-DEA (Figure S5b). The electronic property of P-BT-DEA was further characterized by cyclic voltammetry (CV) measurement (Figure S5c). The LUMO of P-BT-DEA was located at -0.96 V vs. SCE, thus the HOMO was calculated to be 1.23 V vs. SCE according to its optical band gap.

The switchable hydrophilicity and semi-conductive nature of P-BT-DEA allow us to explore water-based photocatalytic reactions. Firstly, the feasibility of P-BT-DEA was demonstrated by photocatalytic degradation of water-soluble organic dyes. In a typical experimental set-up, P-BT-Br, P-BT-DEA, and P-BT-DEA-CO<sub>2</sub> were dispersed in aqueous solution of rhodamine B (RDB) and irradiated under white LED light. As shown in Figure 2a, the hydrophobic P-BT-Br and P-BT-DEA exhibited 17 % and 47.6 % of RDB degradation after 1 h of light exposure, respectively (see Figure S6 for the detailed degradation kinetics). There was a slight enhancement in degradation efficiency with P-BT-DEA than with the original P-BT-Br, which may be attributed to relatively hydrophilic amine group in P-BT-DEA than bromine in P-BT-Br counterpart. Meanwhile, P-BT-DEA-CO<sub>2</sub> exhibited a complete photo-degradation of RDB after 30 min of light irradiation, which is well comparable to a state-of-the-art conducting polymer photocatalyst<sup>[11a]</sup>. It is worth to note that thanks to the high affinity toward water, the P-BT-DEA-CO2 dosage was 10 times lower than the condition of previous studies<sup>[11a, 28]</sup>. Control experiments with P-BT-DEA and P-BT-Br under chemically acidic condition and CO<sub>2</sub>-blown condition, respectively, proved the primary effect

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of hydrophilicity in RDB degradation (Figure S7). The general applicability of P-BT-DEA-CO<sub>2</sub> for dye degradation was then demonstrated via using methylene blue and crystal violet. Similarly, the water-compatible polymer P-BT-DEA-CO<sub>2</sub> showed higher photo-degradation efficiencies than the hydrophobic polymers of P-BT-Br and P-BT-DEA (Figure S8).

P-BT-DEA-CO<sub>2</sub> was subjected to repeated cycles of RDB degradation through CO<sub>2</sub>/N<sub>2</sub> switching. Up to 7<sup>th</sup> cycles, there was no perceptible loss in RDB degradation efficiency, demonstrating a high stability of P-BT-DEA photocatalyst (Figure 2b). The switchable hydrophilicity of the heterogeneous photocatalyst has promoted recovery efficiency as well as water compatibility. Control experiments in the presence of a series of scavengers revealed that reactive species of e<sup>-</sup>, •OH, h<sup>+</sup>, and •O<sub>2</sub><sup>-</sup> played a major role for RDB photo-degradation, well corresponding to previous reports<sup>[29]</sup>. The e<sup>-</sup> scavenger affected the most, decreasing the photo-degradation efficiency down to 51.9 %, since the excited e<sup>-</sup> involves in generating both •O<sub>2</sub><sup>-</sup> and •OH species<sup>[11a]</sup>. When a general radical scavenger was utilized, i.e. vitamin C, the overall degradation efficiency was far deteriorated (Figure S9).



**Figure 2.** (a) Photocatalytic degradation of RDB in a presence of P-BT-Br, P-BT-DEA, and P-BT-DEA-CO<sub>2</sub>.  $C_0$  is initial concentration of RDB after reaching adsorption/desorption equilibrium under dark condition. *C* is the concentration of RDB after light irradiation for a certain time period. (b) Recyclability of P-BT-DEA-CO<sub>2</sub> for repeated degradation of RDB.

The water compatibility of P-BT-DEA-CO<sub>2</sub> was further examined for a variety of organic transformation reactions under visible light; i.e. photo-oxidation, photo-reduction, and photocatalytic heteroaryl-aryl coupling reaction. P-BT-DEA-CO<sub>2</sub> was able to efficiently generate singlet oxygen ( $^{1}O_{2}$ ) (see EPR spectra in Figure S10), thus oxidation reaction through the photogenerated  $^{1}O_{2}$  was carried out. As displayed in Table 1 (Entry 1), 2-furoic acid, well-known as an  ${}^{1}O_{2}$  trap<sup>[30]</sup>, was successfully oxidized into 5-hydroxy-2(5H)-furanone with a conversion of > 99 % for 24 h (see NMR spectra of product in Figure S11). Oxygen gas was applied during the reaction to facilitate  ${}^{1}O_{2}$  generation, and a control experiment in the closed air condition exhibited 35 % of conversion. The P-BT-DEA-CO<sub>2</sub> showed a quantitative conversion of 2-furoic acid up to five repeated cycles, despite of the possible loss of the catalyst by cycles (Figure S12).





Reaction conditions: [a] 2-Furoic acid (1 mmol), P-BT-DEA-CO<sub>2</sub> (0.1 mg mL<sup>-1</sup>), H<sub>2</sub>O (10 mL), r.t., 24 h. Conversion determined by NMR spectroscopy. [b] 4-Nitrophenol (2 mM, 1 mL), P-BT-DEA-CO<sub>2</sub> (0.2 mg mL<sup>-1</sup>), H<sub>2</sub>O (9 mL), NaBH<sub>4</sub> (10 mg), 1 M NaOH (10  $\mu$ L), r.t., 1 h. Conversion calculated by UV-vis spectroscopy. [c] Caffeine (0.3 mmol), 4-methoxybenzenediazonium tetrafluoroborate (0.2 mmol), P-BT-DEA-CO<sub>2</sub> (0.5 mg mL<sup>-1</sup>), H<sub>2</sub>O (10 mL), r.t., 42 h. Conversion observed by GC-MS.

Photo-reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) has been conducted by using P-BT-DEA-CO<sub>2</sub>. As described in Table 1 (Entry 2), the reduction of 4-NP was completed in 1 h of light illumination even with small amount of the catalyst, leading to an average turnover frequency (TOF) of 22.95 h<sup>-1</sup> (see Figure S13a for conversion kinetics, Figure S14 for NMR and GC spectra of product). The P-BT-DEA-CO<sub>2</sub> exhibited a successful conversion of 4-NP over the repeated cycles, resulting in 93 % of conversion efficiency after 3rd cycle (Figure S15). Control experiment showed that no 4-AP was detected in the absence of P-BT-DEA-CO<sub>2</sub>, implying a critical role of photocatalyst for the reduction of 4-NP (Figure S13b). When sodium borohydride (NaBH<sub>4</sub>) was absent, the reduction of 4-NP rarely occurred, rather the degradation of 4-NP took place over time (Figure S13c). This indicates the role of NaBH<sub>4</sub> as essential hydrogen and electron donor<sup>[31]</sup>. The plausible mechanism for the reduction of 4-NP involves electron and proton transfer processes<sup>[32]</sup>. Upon light irradiation, the borohydride was oxidized from photo-induced hole. and at the same time, 4-NP was activated to anionic radical intermediate through the excited electron. The activated substrate extracted the proton from the oxidized borohydride, finally giving 4-aminophenol (4-AP) as a product.

The photo-oxidation and photo-reduction performance of P-BT-DEA-CO<sub>2</sub> prompted us to conduct a reaction involving photoredox catalysis. We then investigated the radical-mediated arylation of heteroarene under visible light to further verify photocatalytic activity of P-BT-DEA-CO<sub>2</sub> in water. As a model reaction, the coupling of caffeine and aryldiazonium tetrafluoroborate was chosen as an important example for the

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direct production of biologically active compounds<sup>[33]</sup> (Table 1 Entry 3). Under the given condition, the cross-coupling product was obtained after 42 h of reaction, giving 85.2 % of conversion efficiency (see NMR spectra of product in Figure S16). Repeating experiments of the heteroaryl-aryl coupling revealed that the P-BT-DEA-CO<sub>2</sub> could be used up to extra five 24 h-cycles without losing the conversion efficiency (Figure S17). When the amount of caffeine was predominant up to 10 equivalents to that of the aryldiazonium counterpart, the conversion efficiency stayed to be 73.4 %. It may be attributed to the lower solubility of excess caffeine in water, where previous studies had to be carried out in harsh acidic condition to dissolve the extra heteroarenes<sup>[33]</sup>. This demonstrates that the utilization of CO2 gas in this work was advantageous in terms of not injecting additional acid, while making the overall condition slightly acidic via formation of carbonic acid in water.

Without light illumination, no coupling product was formed throughout 42 h of experiment. The control experiment in the absence of P-BT-DEA-CO<sub>2</sub> gave a conversion of 9.2 % after 24 h of light irradiation. This may result from the formation of charge-transfer (CT) complex between heteroarene and diazonium ion, generating cross-coupled product<sup>[34]</sup>. The high yield in the presence of photocatalyst indicated that photoredox-induced arylation was still dominant. A plausible mechanism of heteroaryl-aryl coupling is shown in Figure S18. Upon visible light irradiation, 4-methoxybenzenediazonium tetrafluoroborate was activated to form the aryl radical that can be added to caffeine, forming a radical intermediate. Through the oxidation of the radical intermediate with a photo-generated hole, an azacation intermediate was obtained, further resulting in the final cross-coupled product after deprotonation.

In summary, we have demonstrated the  $CO_2$ -reponsive hydrophilicity switch of heterogeneous conjugated polymer photocatalyst containing diethylamine moiety as functional group. The  $CO_2$ -triggered hydrophilicity of the photocatalyst improved catalytic activity in aqueous medium, e.g. for photo-degradation of dyes and organic photo-redox reactions. Furthermore, a simple switch of  $CO_2$  to  $N_2$  facilitated the regeneration of photocatalyst after reaction, leading to the stable cyclic performance. This study marks one of the first attempts to construct water-compatible polymer photocatalyst without compromising its recyclability. We believe our strategy will offer a surfactant-free, facile, and clean route to generate an effective heterogeneous photocatalytic system in water, which paves the way for a variety of environmentally friendly photocatalytic reactions.

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### COMMUNICATION

#### On/Off hydrophilicity of

**photocatalyst**: A tertiary aminetethered conjugated polymer photocatalyst was designed to exhibit a switchable hydrophilicity via a simple  $CO_2/N_2$  trigger. The reversible hydrophilicity of the heterogeneous polymer photocatalyst enhances catalytic efficiency and recyclability for organic photo-redox reactions in water.



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CO<sub>2</sub>-Triggered Switchable Hydrophilicity of Heterogeneous Conjugated Polymer Photocatalyst for Enhanced Catalytic Activity in Water